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**WO 01/57140 A1**

(54) Title: INSULATED NANOSCOPIC PATHWAYS, COMPOSITIONS AND DEVICES OF THE SAME

(57) Abstract: The present invention relates to compositions which provide an insulated nanoscopic pathway. The pathway comprises molecules, polymers or nanoscopic particles capable of conducting charge integrated with nanoscopic switches which are capable of electronic communication with the charge-conducting species. Turning "on" the nanoscopic switch electronically "connects" the various molecules/particles, such that a continuous nanoscopic pathway results. The nanoscopic pathway can be used in a sensor, where the switches can act as receptors for analytes.

carriers responsible for the charge conduction can take an alternative path that avoids the impediments introduced by the bound guests.

One application for nanoscopic pathways is a sensor, particularly for sensing specific molecules. Such sensors include receptor sites to bind analytes via molecular recognition.

5 FIG. 23 shows a schematic of a plurality of isolated receptor molecules 120, each comprising a receptor site 124. Prior to binding analyte 126, receptor molecule 120 has a particular "state" schematically represented by open oval 122, which can define an oxidation state, conformation state, etc. In order to detect a binding event, the sensor relies on a change in the state upon binding an analyte. FIG. 23 schematically shows this change in state with  
10 receptor molecule 130 which is bound to analyte 126 and has a change in state depicted by blackened oval 123. Receptor molecules 120 which do not bind analyte 126 remain in state 122. FIG. 23 depicts a binding event as an equilibrium between a concentration of bound receptors and receptors prior to binding. Sensitivity of the device is thus determined by the equilibrium constant  $K_{eq} = [\text{Bound receptor}]/([\text{Unbound receptor}][\text{Analyte}])$ .

15 The use of conducting polymer films in sensor applications has the potential to increase the sensitivity. FIG. 24 shows a schematic of a polymer film 130 comprising a plurality of individual polymer chains 132. Film 130 spans a dimension 131, which is the dimension between electrodes if incorporated into a device.

FIG. 25 shows a schematic expansion of individual chain 132, in which receptors 142  
20 are incorporated into chain 132 and interspersed between conducting polymer regions 140, i.e. receptors 142 are wired in series. Preferably, the entire chain comprising regions 140 and 142 comprise a continuous conducting pathway. Each receptor has a site 144 with an initial state depicted by open oval 143. Upon binding analyte 146, the state 146 of each receptor site 142 is affected due to the electronic communication existing between each receptor site  
25 142. The result is a large signal amplification. Only a fractional occupancy is required to achieve a collective signal response.

Despite such recent improvements, there still exists a need to improve the signal amplification for sensors requiring even heightened sensitivity. There also exists a need to develop new nanoscopic materials and materials systems.

Another aspect of the present invention provides a method for detecting the presence of an analyte, comprising the step of providing an article comprising a nanoscopic pathway. The method further comprises the steps of positioning a plurality of nanoscopic switches along the nanoscopic pathway, and deactivating a number of the plurality of nanoscopic switches, the number being less than a percolation threshold.

Another aspect of the present invention provides a method for synthesizing a conducting polymer comprising the step of providing a monomer having a first and second polymerization site. The method further comprises the steps of polymerizing the monomer at the first site to produce a first polymer, and polymerizing the monomer at the second site to produce a second polymer, the second polymer isolating the first polymer.

Another aspect of the present invention provides a block co-polymer, comprising blocks of a conducting material and blocks of a dielectric material. The blocks are arranged such that the blocks of the conducting material form a nanoscopic pathway insulated by blocks of the dielectric material.

Other advantages, novel features, and objects of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings, which are schematic and which are not intended to be drawn to scale. In the figures, each identical or nearly identical component that is illustrated in various figures is represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention.

#### **Brief Description of the Drawings**

FIG. 1 shows a schematic cross-section of an article having a nanoscopic pathway isolated by a dielectric and including nanoscopic switches;

FIG. 2A shows a schematic cross-section of a multi-stranded polymer having a central conducting polymer strand isolated by multiple dielectric polymer strands, the multi-stranded polymer including nanoscopic switches;

FIG. 2B shows a central conducting polymer isolated by a single dielectric polymer;

potential of the same films at a sweep rate of  $5 \text{ mVs}^{-1}$  with a 40 mV offset potential between adjacent electrodes;

FIG. 13 shows a schematic representation of the participation of the Cu ion in the nanoscopic pathway;

5        FIG. 14 shows a schematic representation of the synthesis of iptycene-containing phthalocyanine monomers: (a) 2 equiv of  $\text{Br}_2$ ,  $\text{CHCl}_3$  rt (87%); (b) 4 equiv of  $\text{Na}_2\text{S}_2\text{O}_4$ , 1:1  $\text{Et}_2\text{O}:\text{H}_2\text{O}$ , rt (90%); (c) 5 equiv of  $\text{K}_2\text{CO}_3$ , 8 equiv of  $(\text{CH}_3)_2\text{CHBr}$ , DMF,  $60^\circ\text{C}$ , 3 d (93%); (d) 6 equiv of  $\text{CuCN}$ , DMF,  $140^\circ\text{C}$ , 3 d (71%); (3) cat. Na,  $\text{NH}_3$  (g), ethylene glycol,  $140^\circ\text{C}$ , 5 h (87%); (f) 4-iodophthalonitrile,  $\text{Mg}(\text{OBu})_2$ , BuOH, reflux, 1 d; (g)  $\text{M}(\text{acac})_2$ , THF, reflux, 1 d; (h)  $\text{Bu}_3\text{EnEDOT}$ ,  $\text{PdCl}_2(\text{PPh}_3)_2$ , DMF,  $60^\circ\text{C}$ , 1 d;

FIG. 15 shows cyclic voltammograms (solid lines) and conductivity profiles (dashed lines) of (a) poly(9-Co) and (b) poly(9-Ni) in 0.1 M  $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$  on  $2 \mu\text{m}$  interdigitated microelectrodes. Sweep rates are 100 mV/s for cyclic voltammograms and 5 mV/s with a 40 mV offset potential for conductivity measurement;

15        FIG. 16 shows cyclic voltammogram (solid line) and conductivity profile (dashed line) of poly(8-Co) in 0.1 M  $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$  on  $2 \mu\text{m}$  interdigitated microelectrodes. Sweep rates and offset potentials were the same as in FIG. 15;

FIG. 17 shows cyclization of  $\alpha$ -linked and  $\beta$ -linked species;

FIG. 18 shows electropolymerization (a) of the monomer: The dashed line is the first sweep and the increasing current with successive sweeps indicates that polymerization occurs; the cyclic voltammetric behavior of the thin film (b) on a  $2 \text{ mm}^2$  platinum button electrode shows reversible electrochemical behavior, (scan rates were 100 mV/s);

FIG. 19 shows examples of  $\alpha$ -linked and  $\beta$ -linked tetrathienyl monomers;

FIG. 20 shows more monomers and polymers of the present invention;

25        FIG. 21 shows space-filling model of 60 (a) and an octamer of poly1-L (b);

FIG. 22 shows a schematic of a prior art device incorporating a polymer film capable of conducting charge;

FIG. 23 shows a schematic of an equilibrium between a plurality of isolated, unbound receptors and a plurality of receptors after being exposed to an analyte;

30        FIG. 24 shows a schematic of a polymer film capable of conducting charge comprising a plurality of individual polymer chains;

polythiophene, polypyrrole, polyphenylene, polyarylene, poly(bisthiophene phenylene), a conjugated ladder polymer, polyiptycene, polytriphenylene, poly(arylene vinylene), poly(arylene ethynylene), the corresponding monomers, corresponding oligomers and organic and transition metal derivatives thereof. Typical organometallic or coordination compounds in a nanoscopic pathway include metals capable of delocalizing charge through bound ligands. A variety of such compounds are known in the art. Silicon nanowires can also be contemplated for use in a nanoscopic pathway.

In one embodiment, electronic charge can occur via charge transfer (electron "hopping") between redox-active centers. "Redox-active" refers to a metallic, organic, organometallic or metal ion species capable of accepting or donating electronic charge. The charge transfer need not necessarily occur between two species having orbital overlap, and can occur via a long range charge transfer mechanism. Charge transfer can include a transfer of negative charge (e.g. an electron) or positive charge (e.g. a hole). For example, a nanoscopic pathway can be provided from a collection of nanoparticles, i.e. particles having at least one dimension less than about 1  $\mu\text{m}$  which are arranged in electronic communication with each other. The particles are capable of conducting electronic charge either via a charge transfer mechanism or even through physical contact between the particles. In yet another embodiment, the nanoscopic pathway can involve a combination of redox-active species in conjunction with a conjugated pathway. In still another embodiment the nanoscopic pathway can comprise species with metallic properties (e.g. having a conducting mechanism similar to a metallic wire), for example species that do not have localized redox centers and hopping conduction.

FIG. 26 shows an idealized diagram of a device having a molecular wire polymer incorporating receptor sites, in which the molecular wire comprises a nanoscopic pathway (e.g. poly(thiophene) or poly(pyrrole)) extending between two electrodes, allowing the resistance to be measured. The distance between the electrodes defines the path length of the nanoscopic pathway. In FIG. 26, device 150 comprises film 155 of a molecular wire polymer deposited on substrate 151 between electrodes 152 and 153. An electrical circuit 154 capable of determining the resistance with voltmeter (or ammeter) 157 completes device 150. Film 155 comprises receptor sites 156a-e interspersed between conjugated chains 158. Site 156d is shown as bound to analyte 159. Energy along the nanoscopic pathway, depicted as line 160, increases as shown in the direction of the arrow adjacent the label "E". Binding of

In one embodiment, the article includes a nanoscopic switch. The article can have one nanoscopic switch per nanoscopic pathway, or a plurality of switches per nanoscopic pathway. The switch is a chemical or biological species capable of altering the conductivity of the nanoscopic pathway. The nanoscopic switch can be positioned anywhere in the article, e.g. in the nanoscopic pathway, in the dielectric, along an interface of the dielectric and the nanoscopic pathway. "Altering" can involve either reducing or increasing the conductivity of the nanoscopic pathway. "Altering" can also involve completely shutting down the conduction, or turning the conduction "on" from an initially "off" state. Thus, the nanoscopic switch can mediate charge transfer (or conduction) through the pathway. In one embodiment, the switch is redox-active, allowing it to participate in charge transfer, oxidation or reduction processes.

In one embodiment, the nanoscopic switch is redox active. In one embodiment, the nanoscopic switch is capable of mediating electronic charge via a tunneling mechanism. In the situation where a material exhibits high conductivity, electronic charge can travel through a pathway while experiencing relatively low energy barriers. "Tunneling" refers to a transfer of charge through a region having a high energy barrier.

In one embodiment, the nanoscopic switch is capable of mediating charge via a chemical reaction. For example, the addition or removal of charge from a nanoscopic switch can result in the loss, formation, displacement or transfer of a chemical bond.

One embodiment of an article of the present invention is shown schematically in FIG. 1. FIG. 1 shows a cross-section of article 2 having a nanoscopic pathway 4 having a minimum dimension 5. Pathway 4 can comprise one continuous molecule or an interconnected series of molecules and/or nanoparticles. Nanoscopic pathway 4 is isolated by a dielectric 6. Dielectric 6 has a high resistance, and can be a vacuum, a gas, a liquid or a solid material. Nanoscopic switches 8 can be positioned anywhere in the article so long as it serves to alter the conductivity of nanoscopic pathway 4. The various positions of nanoscopic switches 8 shown in FIG. 1 illustrates at least some of the possible positions of the nanoscopic switch in the article, and is not meant to indicate that the article must possess nanoscopic switches in all these positions. If desired, the article can include a plurality of more than one type of nanoscopic switches in any position.

In one embodiment, the nanoscopic switch operates by a change in conformation. Typically, a significant portion of the switch comprises an organic group capable of changing

second polymers can be attached by attachment 25 which can comprise a chemical bond, or an intermediary chemical species (e.g. an organic group, a metal ion, a metal ion complex) or biological species. Nanoscopic switches 28 can be interspersed throughout the first polymer 24. Alternatively, attachment 25 can comprise a nanoscopic switch. FIG. 3(b) illustrates an aggregate of double-stranded polymers 20. Preferably the aggregate is anisotropic in which the nanoscopic pathways have substantially the same orientation. The aggregate does not necessarily have to provide a linear pathway and can be curved, as demonstrated by double-stranded polymer 20. The aggregate can comprise nanoparticles or any article comprising a dielectric and nanoscopic pathway, as schematically illustrated in FIGs. 1 and 2.

In one embodiment, nanoparticles making up the nanoscopic pathway have anisotropic character, i.e. have an aspect ratio of greater than 5. In another embodiment, nanoparticles include nanotubes, metal clusters, semiconductor clusters, colloids and fibers. A minimum dimension of these particles can be that of the nanoscopic pathway, i.e. less than about 20 nm and preferably less than about 10 nm.

Nanotubes can be composed of  $sp^2$  carbon atoms bonded exclusively to each other and arranged to enclose a hollow cavity. Carbon nanotubes are known to have conductivity properties. Other examples of nanotubes include metallized nanotubes, which comprise a metal coating over an organic substance. For example, a biological species (e.g. a lipid, a virus such as tobacco mosaic virus) or a chemical species (e.g. a surfactant) can provide a template for metallization, i.e. a process for depositing a metal coating on a template. Thus, a thin metal coating in the shape of a hollow vessel, such as a tubule, can be formed having dimensions of less than about 20 nm, or any dimension sufficient to provide a nanoscopic pathway having dimensions as described herein. Examples of such metallization are described in Schnur, Science Vol. 262(5140), p. 1669-1676 (1993) or Chow et al., Materials Science and Engineering A, Vol. 158(1), p. 1-6 (1992), each of which are incorporated herein by reference in its entirety.

Metal clusters and colloids comprise aggregates of metal atoms, such as gold, copper and silver. A typical minimum dimension of a cluster or colloid is about 2 nm. Colloids are typically dispersed in a second, host phase. In addition, a collection of colloids can adhere to each other to produce colloidal aggregates. Semiconductor clusters typically comprise binary inorganic compounds such as metal halides, metal oxides, metal sulfides, metal chalcogenides, and III-V semiconductors. Examples include CdO, CdS, CdSe, CdTe, ZnO,

crystal phase can be a lyotropic liquid crystal (e.g. sodium dodecylsulfate, a phospholipid membrane), which requires the addition of solvent to provide anisotropic orientation of the liquid crystals. The liquid crystal phase can be thermotropic, as displayed by, for example, 5CB (pentyl substituted cyanobiphenyl). The liquid crystalline phases can further be used  
5 align the nanoscopic pathways to create optimal isolation and positioning of the switching elements.

In one embodiment, the nanoscopic switch and the nanoscopic pathway are capable of being redox-matched. "Redox-matched" refers to a situation where a difference in redox potentials between the nanoscopic pathway and the nanoscopic switch is minimized. In one  
10 embodiment, the nanoscopic switch and nanoscopic pathway are each redox-active. A "redox potential" refers to an electrochemical potential required to effect charge transfer either to and from the redox-active components. When at least one component is conducting and exhibits a maximum conductivity at a particular redox-potential or redox-potential range, redox-matching allows an optimal mixing of electronic states of the conductor with electronic  
15 states of its redox-matched partner, thereby enhancing electronic communication. The enhanced electronic communication can increase conductivity. In one embodiment, redox-matching can be achieved by altering a chemical property of either the nanoscopic switch or the nanoscopic pathway. For example, the nanoscopic switch and the pathway may undergo redox-chemistry at different electrochemical potential ranges. In an examples where the  
20 nanoscopic switch comprises a coordination compound, altering the electron-donating properties of the ligand can shift the electrochemical potential range to match that of the nanoscopic pathway. In another example, the nanoscopic pathway can be derivatized with groups having electron-poor or electron-rich properties, such that the pathway has an electrochemical potential range matching that of the nanoscopic switches. Redox-matching  
25 and examples of redox-matching is discussed further in co-pending U.S. Application Ser. No. 09/201,743, to Swager et al. entitled "Conducting Polymer Transition Metal Hybrid Materials and Sensors," filed December 1, 1998, which is incorporated herein by reference.

In one embodiment, the a nanoscopic pathway is a conductor within a defined electrochemical potential range. This type of pathway requires an input of electrochemical  
30 energy to afford conduction. In one embodiment, this pathway is non-conducting outside of this defined electrochemical range. In one embodiment, the nanoscopic pathway comprises a first nanoscopic pathway and is a conductor within a first electrochemical potential range.



charge) conduction cannot occur throughout pathway 4 in the direction of arrow 5. If the nanoscopic switch is capable of detecting an analyte, a binding event between the nanoscopic switch and the analyte will alter the electronic properties of the nanoscopic switch and allow at least some conduction to occur through pathway 4. Of course, this is one extreme example, and the nanoscopic switch can alter conductivity simply by increasing or reducing conduction, for example, such as optimizing or decreasing an amount of orbital overlap between the nanoscopic switch and the pathway. In one embodiment, the sensor includes a plurality of nanoscopic pathways arranged in parallel to each other. Such an arrangement can provide the sensor with an increased signal.

10 Another aspect of the present invention provides a composition comprising a nanoscopic pathway and a polymer isolating the nanoscopic pathway. In one embodiment, the nanoscopic pathway is a conducting polymer, such as any conducting polymer disclosed herein. The polymer isolating the nanoscopic pathway can be a dielectric polymer, such as any dielectric polymer disclosed herein. In one embodiment, the composition comprises a  
15 multi-stranded polymer. FIG. 2 schematically illustrates a multi-stranded polymer. In Fig. 2, the nanoscopic pathway is represented as a central conducting polymer. One or more dielectric polymers

In one embodiment, the dielectric polymer is attached to the conducting polymer. For certain examples, this attachment provides a rigidity that maintains the integrity of the  
20 nanoscopic pathway, perhaps by preventing chain entanglement. The attachment can also be a result of the polymerization of a monomer having two polymerization sites (described below). In one embodiment, the dielectric polymer is attached to the conducting polymer via a chemical bond.

One method for attaching a dielectric polymer to the conducting polymer is by  
25 providing a structure comprising the formula:

separated structure 50, where regions 54 comprise an alignment of conducting blocks whereas regions 56 comprise an alignment of dielectric blocks. This structure provides an arrangement in which the conducting blocks allow conduction throughout an entire block (by conjugation, redox conductivity, or a combination thereof). In addition, the conducting blocks are insulated by dielectric blocks. Depending upon the ratio of the compositions of each block the conducting block can be organized into layered structures or a hexagonal array of columns. The block copolymer can be a diblock, a triblock, or any multiblock copolymer as known in the art.

In one embodiment, dielectric blocks are selected from the group consisting of polyolefins, polyesters, polyamides, polyarylenes, polyethers, polyketones, polyarylsulfides, fluoropolymers, polyacrylates, polymethacrylates, polysiloxanes, polystyrene, polyurethanes, proteins and derivatives thereof. In one embodiment, conducting blocks comprise conjugated organic groups, nanoparticles or a combination thereof. For example, the conducting blocks can be a conducting organic group, such as an organic group selected from the group consisting of polyaniline, polythiophene, polypyrrole, polyphenylene, polyarylene, poly(bisthiophene phenylene), a conjugated ladder polymer, polyiptycene, polytriphenylene, poly(arylene vinylene), poly(arylene ethynylene), and organic and transition metal derivatives thereof. The conducting block can comprise a gel.

Examples of block copolymers are presented in FIGs. 6-9.

FIG. 9 are examples of monomers in a polymer that can bind to metal ions or nanoparticles such as semiconductor nanoparticles.

In one embodiment, the activating step can involve redox-matching the nanoscopic pathway with the nanoscopic switch. In another embodiment, the activating comprises adjusting an electrochemical potential applied to the nanoscopic pathway. In these embodiments, the nanoscopic switch is a part of the nanoscopic pathway.

Another aspect of the invention provides an article comprising a percolation network. A "percolation network" is a lattice comprising a random mixture of conducting and non-conducting links. A "percolation threshold" is a minimum concentration of conducting links necessary to generate a conduction pathway between two sites situated within the percolation network. In one embodiment, the conducting links comprise sub-nanoscale pathways in themselves, albeit of a smaller scale. Positioned amongst these sub-nanoscale pathways are a plurality of nanoscopic switches which, when unactivated, are the non-conducting links.

the two species, providing a more optimal conduction pathway. Redox-matching can be provided by any method described herein.

In one embodiment, the activating step involves applying an electrochemical potential to the nanoscopic pathway. This may be necessary where the nanoscopic pathway is  
5 conducting within a particular electrochemical potential range.

Another aspect of the present invention provides a method for detecting the presence of an analyte. The method involves providing an article comprising a nanoscopic pathway having a conductivity and insulating the nanoscopic pathway. The method also involves  
activating detection sites positioned in the article.

10 In one embodiment, the activating comprises a binding event between the analyte and the detection site. In one embodiment, the binding event causes the detection site and the pathway to be redox-matched, thus increasing or reducing the extent of conduction in a detectable manner. In one embodiment, the detection site comprises a metal ion complex (e.g. a coordination compound, an organometallic compound). In one embodiment, the  
15 analyte is a potential ligand which can bind to the metal ion of the complex. In another embodiment, the metal ion complex has a ligand which can bind other analyte ligands, either covalently, ionically, sterically (e.g. a cage or pseudo-cage). In one embodiment, the analyte is a metal ion and the metal ion complex has a ligand (e.g. a crown ether, a macrocycle, etc.) which can bind the analyte metal ion.

20 In one embodiment, DNA comprises a detection site. The analyte can be any biological species capable of binding to DNA, such as a complementary strand of DNA or RNA.

Another aspect of the present invention provides a method for amplifying conductivity. The method involves providing an article comprising a nanoscopic pathway  
25 and positioning a plurality of nanoscopic switches in the article. A number of the plurality of nanoscopic switches, the number being less than the total value of nanoscopic switches, is activated where the number is greater than a percolation threshold.

Another aspect of the invention a method for reducing conductivity. The method involves providing an article comprising a nanoscopic pathway and positioning a plurality of  
30 nanoscopic switches in the article. In this aspect, a number of the plurality of nanoscopic switches is deactivated such that the number is less than a percolation threshold.

One aspect of the present invention provides a method for synthesizing a conducting

interdigitated array microelectrodes purchased from AAI-ABTECH with an interelectrode spacing of 5  $\mu\text{m}$ , with a platinum coil counter electrode and an isolated Ag wire quasi-reference electrode. All the potentials are reported versus the  $\text{Fc}/\text{Fc}^+$  redox couple.

Compound 6 was synthesized from the tosylate (Q. Zhou, T.M. Swager, *J. Am. Chem. Soc.*, 1995, 117, 12593) by simple exchange with iodide ion and 7 was produced synthesized as reported previously (C.O. Dietrich-Buchecker, J.-P. Sauvage, *Tetrahedron Lett.* 1983, 24, 5091). Macrocycle 64 was produced by straight forward adaptation of conditions used for the synthesis of related macrocycles (C.O. Dietrich-Buchecker, J.-P. Sauvage, *Tetrahedron Lett.* 1983, 24, 5091).

Additional experimental details can be found in a paper entitled "Three-Strand Conducting Ladder Polymers: Two-Step Electropolymerization of Metallorotaxanes", by J. Buey and T.M. Swager (*Angew. Chem. Int. Ed.* 2000, 39, No. 3, 608-612), which is herein incorporated by reference in its entirety.

#### Example 2

Synthesis of 63 (see FIG. 10): Compound 64 (100 mg, 0.115 mmol), 2-(tributylstannyl)-3,4 ethylenedioxythiophene (124 mg, 0.288 mmol), CuI (66 mg, 0.346 mmol) and  $t\text{-PdCl}_2(\text{PPh}_3)_2$  (4 mg) were dissolved in 10 mL dry DMF and the mixture was stirred overnight at 80°C. The DMF was then evaporated and the residue was extracted with  $\text{CH}_2\text{Cl}_2/\text{NH}_4\text{OH}$ . The organic phase was dried and the crude product was precipitated with hexane. Column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  99:1) afforded the desired compound as a yellow solid in 90% yield.

#### Example 3

Synthesis of Monomer 60 (see FIG. 10): A solution of  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$  (5.3 mg, 0.017 mmol) in dry deoxygenated MeCN (2 mL) was transferred via cannula to the solution of 62 (8 mg, 0.017 mmol) and 63 (15 mg, 0.017 mmol) in 10 mL dry deoxygenated dichloromethane. After 3 h stirring the solvents were evaporated and the residue was dissolved in acetone and filtered. Evaporation to small volume and addition of diethylether afforded compound 60 as a green powder in 60% isolated yield.

voltammograms indistinguishable from those obtained from poly4, as is consistent with polymerization. The cyclic voltammogram of poly1 (FIG. 11) is also similar but contains an added  $\text{Cu}^{1+/2+}$  wave centered at 0.11 V vs.  $\text{Fc}/\text{Fc}^+$ . The UV-vis spectra also supports the selective polymerization of the macrocyclic ligand, and both poly1 and poly2 displayed absorption spectra similar to that of poly4 ( $\lambda_{\text{max}} = 503 \text{ nm}$ ) with an additional absorption feature at about 450 nm assigned to the threading ligand, 62.

#### Example 6

Synthesis of poly1-L and poly2-L (see FIG. 10): Subjecting deposited films of poly1 or poly2 to higher potentials in monomer-free electrolyte resulted in the polymerization of the 4,4'-bis(dithienyl)-2,2'-bipyridine threading ligand to form ladder polymers poly1-L and poly2-L, respectively. This process is readily apparent from FIG. 11 wherein the first sweep to 1 V vs.  $\text{Fc}/\text{Fc}^+$  results in a large irreversible oxidation current. This irreversible current is expected since oxidation of the threading ligand, 62, will produce radical cations that undergo intermolecular coupling with loss of protons to form new thiophene-thiophene linkages (i.e. polymerization). The second sweep over the same expanded potential range lacks this irreversible oxidation and is identical to all subsequent sweeps.

The efficiency of the second polymerization can be deduced from an analysis of the irreversible charge relative to the reversible charge. A key parameter is the mass of the polymer immobilized on the electrodes. Once the mass of the polymer has been determined, the degree of oxidation of the polymer is also known. This analysis was afforded by a comparison of poly1, poly2, and poly4. Due to the fact that the metal ions do not directly interact with the macrocyclic polymer's electronic structure, poly2 and poly4 have nearly identical cyclic voltammetric responses over the potential region of  $-0.5$ - $0.55 \text{ V}$  vs.  $\text{Fc}/\text{Fc}^+$  and display the same number of Coulombs per gram of polymer deposited. Poly1 has an additional one electron  $\text{Cu}^{1+/2+}$  wave in that potential region, which also serves as an internal standard to establish the moles of polymer repeating units in the film.

It can be seen that poly1, poly2, and poly4 are respectively oxidized by 3.2, 2.2, and 2.2 electron per repeating unit when cycled to  $0.55 \text{ V}$  vs.  $\text{Fc}/\text{Fc}^+$ . With regard to the efficiency of the second polymerization of poly1 and poly2, the respective irreversible charge passed was 1.7 and 2.1 electron per repeating group. A quantitative polymerization results in 2 electrons per monomer being removed irreversibly. After the first sweep to high potential a

clear match of the polymer lengths, and the chain of poly4 is incarcerated between two strands of poly3. An additional feature revealed by the structure is the steric constraints of the phenanthroline portion of the macrocycle. This unit presents a rigid steric barrier that prevents close contacts between neighboring polymers and thereby promotes intrapolymer coupling in the second polymerization to favor the three-strand ladder structure.

Comparisons of the conductivity and electrochemistry (FIG. 12) of poly1-L, poly2-L, and poly4 provide evidence that the internal polymer behaves as a partially isolated wire when the outer two polymer-strands are in their insulating (undoped) state. The observed electroactivity has three components; (1) the macrocyclic polymer, (2) the Cu center (for poly1-L), and (3) the threading polymer. A comparison with poly4 (FIG. 12) indicates that the first wave at about 0.1 V vs.  $\text{Fc}/\text{Fc}^+$  and a broad featureless electroactivity at more positive potentials for poly1-L and poly2-L can be assigned to the macrocycle-containing polymer. For poly1-L the  $\text{Cu}^{1+/2+}$  wave overlaps the macrocyclic polymer's electroactivity, which creates an optimal situation for the Cu-centered electroactivity to enhance the conductivity.

The conductivities of rotaxane complexes of poly3 have been previously determined to be low (ca.  $10^{-3}$  S/cm), and thus the poly4 backbone is the dominant contributor to the conductivity of the ladder polymers. Simple inspection of FIG. 21 reveals that the conductivity ( $\sigma$ ) of poly1-L (to obtain conductivities the coverage on the electrodes were determined by profilometry and are related to the conductivity of poly(3-methylthiophene),  $\sigma = 60 \text{ S cm}^{-1}$  to correct for non-uniform coverage – this method has been established to provide a reliable measurement of a number of electropolymerizable monomers. R.P. Kingsborough, T.M. Swager, *Adv. Mater.* 1998, 10,1100; G. Zotti, G. Schiavon, *Synth. Met.* 1990, 39, 183; G. Schiavon, S. Sitran, G. Zotti, *Synth. Met.* 1989, 32, 209) at 0.25 V vs.  $\text{Fc}/\text{Fc}^+$  is 38  $\text{S/cm}^{-1}$ ), is approximately 20 times higher than poly2-L at the same potential ( $\sigma = 2 \text{ S/cm}$ ). Likewise, the conductivity of poly4 at the same potential is 66  $\text{S/cm}^{-1}$ . All three materials poly1-L, poly2-L, and poly4 display comparable (within a factor of 2) conductivities at high potentials ( $\sim 0.9 \text{ V vs. Fc}/\text{Fc}^+$ ). These conductivity comparisons demonstrate that the central macrocyclic polymer (poly4) in poly1-L and poly2-L is isolated by the outer polymers (poly3 chains) when they are in their insulating states. When the poly3 chains are insulating, the Cu ion's electroactivity can assist in interchain transport. The Cu ion's redox potential is optimally positioned to participate in the conduction. This effect, illustrated in FIG. 13 (poly3 chains comprising macrocycle 70 and chain 72 and poly4 chain

7389; E.W. Paul, A.J. Ricco, M.S. Wrighton, *J. Phys. Chem.* 1985, 89, 1441; J.W. Thackeray, H.S. White, M.S. Wrighton, *J. Phys. Chem.* 1985, 89, 5133; D. Ofer, R.M. Crooks, M.S. Wrighton, *J. Am. Chem. Soc.* 1990, 112, 7869), results in the deposition of dark green films of poly(9-Co) and poly(9-Ni). The polymerization proceeds by oxidative coupling of the pendant thiophenes (FIG. 14). The cyclic voltammogram of these polymers in fresh (monomer free) electrolyte on the interdigitated microelectrodes (Pt button electrodes give identical results) is shown in FIG. 15a. Films of poly(9-Co) are characterized by a wave at -0.6 V vs Fc/Fc<sup>+</sup> (Unless noted all potentials are referenced to the Fc/Fc<sup>+</sup> redox couple), which is attributed to the Co<sup>1+/2+</sup> redox process, followed by a very broad region of redox activity. This broad nature suggests overlapping or admixed redox processes (i.e. redox matched), including the Co<sup>2+/3+</sup> redox wave, a ligand-based oxidation, and EDOT-based electrochemistry. The conductivity profile is observed to increase at potentials corresponding to the Co<sup>2+/3+</sup> redox wave, suggesting that the metal centered redox activity contributes to the conductivity, and finally reaches a maximum at 0.35 V. The low hysteresis in the conductivity and voltammogram suggests that minimal structural reorganization accompanies the redox cycling. Using methods described previously (R.P. Kingsborough, T.M. Swager, *Adv. Mater.* 1998, 10, 1003; R.P. Kingsborough, T.M. Swager, *J. Am. Chem. Soc.* 1999, 121, 8825), a maximum conductivity of approximately 40 S/cm is obtained.

Poly(9-Ni) displays new features in the reductive region at -1.35 V and -1.75 V (FIG. 15b). Based upon comparisons of cyclic voltammograms with those of the *cis* derivative, 8-Ni, the first one-electron wave is assigned to a Ni<sup>1+/2+</sup> redox process and the second to a ligand-centered process. In the oxidative region, the cyclic voltammogram of poly(9-Ni) consists of a single broad redox wave centered at 0.3 V with a leading shoulder at 0.1 V. The higher oxidation potential required for electroactivity of poly(9-Ni) compared to poly(9-Co) is not unexpected since it lacks the lower potential Co<sup>1+/2+</sup> and Co<sup>2+/3+</sup> redox waves. The *in situ* conductivity trace (FIG. 15b) shows redox conduction associated only with the polymer backbone and not the metal-centered and ligand-centered reductive processes. The Co<sup>1+/2+</sup> wave, which is not redox-matched, produces no conductivity in poly(9-Co). The maximum conductivity is observed at the half-wave potential of the polymer film ( $\sigma_{\max} = 30$  S/cm) and decreases rapidly at higher applied potentials.

is also degrading. These films can be stable in aqueous media, a feature relevant to ascertain stability in ambient conditions. The crown ether linkages bind metal ions and change the redox potential of segments of the polymer and thereby constitute a switching mechanism.

The  $\beta$ -linked tetrathienyl monomer of FIG. 19 displays very desirable electrochemical behavior and is readily electropolymerized into thin highly conductive films. The added solubility of the hexyl sidechains can make soluble analogs. The  $\alpha$ -linked monomer undergoes an irreversible oxidation at 0.9 V vs. Ag/Ag<sup>+</sup> suggestive of a cyclization and/or polymerization. Due to the higher solubility no film deposition was observed. The model compound displays reversible redox wave in CH<sub>2</sub>Cl<sub>2</sub> electrolyte at  $E^{1/2} = 1.25$  V vs. Ag/A.

#### Example 11

Electron-rich macrocyclic monomers can be polymerized about electron-poor template polymers as shown in FIG. 20. Polyrotaxane 82 can be produced by either polymerizing rotaxane monomer (pathway A, comprising electron rich macrocycle 80 and electron poor templating polymer 81) or by assembling macrocycle 80 around an existing templating polymer 81. In the simplest case, the macrocycle 80 will have coupling sites 80a and 80b and polymers with structures schematically shown as 83 or 84 will be formed. This polymer is a ladder polymer by virtue of the fact that to completely sever the polymer backbone two bonds must be broken. However the strong covalent bonds are on two different polymers held together by non-covalent interactions. Few such synthetic ladder polymers have been previously synthesized. Non-covalent ladder polymers in biological species and related assemblies can also be used (e.g. DNA, beta-sheets). Macrocycles containing four coupling sites can create three strand ladder polymers 84.

Monomer 90 can function as the electron poor element. This choice is based upon the fact that the diol structure is readily converted to a number of polymeric structures (e.g. polyesters, polysiloxanes, etc.) by standard methods. Great flexibility can be provided in the choice of a linking group. Linking groups that can be readily cleaved will allow for the electron poor templating polymer to be removed. Removal of the template in 84 can generate a tubular structure which can be subsequently utilized for the transport/binding of ions or small molecules to produce separation/sensory materials. Furthermore the binding of



Claims

1. An article comprising:  
a nanoscopic pathway having a conductivity;  
5 a dielectric insulating the nanoscopic pathway; and  
a nanoscopic switch in electronic communication with the nanoscopic pathway being  
capable of altering the conductivity of the nanoscopic pathway.
2. The article of claim 1, wherein the nanoscopic pathway comprises an organic group.
- 10 3. The article of claim 2, wherein the nanoscopic pathway comprises a conducting  
polymer.
4. The article of claim 3, wherein the conducting polymer is selected from the group  
15 consisting of polyaniline, polythiophene, polypyrrole, polyphenylene, polyarylene,  
poly(bisthiophene phenylene), a conjugated ladder polymer, polyiptycene, polytriphenylene,  
poly(arylene vinylene), poly(arylene ethynylene), and organic and transition metal  
derivatives thereof.
- 20 5. The article of claim 3, wherein a portion of the conducting polymer comprises a  
multi-dentate ligand.
6. The article of claim 3, further comprising a metal ion bonded to a portion of the  
conducting polymer.
- 25 7. The article of claim 1, wherein the nanoscopic pathway comprises a pathway of  
nanoparticles.
8. The article of claim 7, wherein the nanoparticles are selected from the group  
30 consisting of nanotubes, metal clusters, semiconductor clusters, colloids and fibers.

20. The article of claim 19, wherein the dielectric polymer is selected from the group consisting of polyolefins, polyesters, polyamides, polyarylenes, polyethers, polyketones, polyarylsulfides, fluoropolymers, polyacrylates, polymethacrylates, polysiloxanes, polystyrene, polyurethanes, proteins and derivatives thereof.

5

21. The method of claim 19, wherein the dielectric polymer comprises a gel.

22. The article of claim 19, wherein the dielectric polymer is attached to the conducting polymer.

10

23. The article of claim 22, wherein the dielectric polymer is attached to the conducting polymer via a chemical bond.

24. The article of claim 23, wherein the dielectric polymer is chemically bonded to the  
15 conducting polymer via a metal ion.

25. The article of claim 18, wherein the ceramic is selected from the group consisting of a metal oxide and a mixed metal oxide.

20 26. The article of claim 25, wherein the ceramic is a silicate.

27. The article of claim 26, wherein the silicate is a porous silicate.

28. The article of claim 1, wherein the dielectric comprises a biological species.

25

29. The article of claim 1, wherein the dielectric includes a metal ion.

30. The article of claim 1, wherein at least a portion of the nanoscopic pathway or the dielectric comprises a block co-polymer.

30

39. The article of claim 1, wherein the nanoscopic switch is positioned in the nanoscopic pathway.

40. The article of claim 1, wherein the nanoscopic switch and the nanoscopic pathway are  
5 capable of being redox-matched.

41. The article of claim 1, wherein the nanoscopic switch is redox-active.

42. The article of claim 1, wherein the nanoscopic switch is a metal ion.

10 43. The article of claim 1, wherein the nanoscopic switch comprises a biological species selected from the group consisting of DNA and a redox-active enzyme.

44. The article of claim 3, wherein the nanoscopic switch is attached to a portion of the  
15 conducting polymer.

45. The article of claim 1, wherein the nanoscopic switch is capable of being activated to alter the conductivity of the nanoscopic pathway.

20 46. The article of claim 45, wherein the nanoscopic switch is capable of altering the conductivity upon binding to an analyte.

47. The article of claim 1, wherein the nanoscopic pathway is a conductor within a first electrochemical potential range.

25 48. The article of claim 47, wherein the nanoscopic pathway is a first nanoscopic pathway, and the dielectric comprises a second nanoscopic pathway.

49. The article of claim 48, wherein the second pathway is a conductor within a second  
30 electrochemical potential range.

nanoscopic switch means in electronic communication with the nanoscopic pathway being capable of altering the conductivity of the nanoscopic pathway

60. An article comprising:

- 5 means for conducting electronic charge along a nanoscopic pathway;  
a dielectric insulating the nanoscopic pathway; and  
nanoscopic switch means in electronic communication with the nanoscopic pathway being capable of altering the conductivity of the nanoscopic pathway.

10 61. A method for altering conductivity, comprising:

providing an article comprising a nanoscopic pathway having a conductivity;  
insulating the nanoscopic pathway; and  
activating a nanoscopic switch positioned in the article.

15 62. The method of claim 61, wherein the nanoscopic switch is positioned in the nanoscopic pathway.

63. The method of claim 61, wherein the nanoscopic switch comprises redox-active species.

20

64. The method of claim 61, wherein the nanoscopic switch comprises a metal ion.

65. The method of claim 61, wherein the nanoscopic switch comprises a biological species.

25

66. The method of claim 61, wherein the activating comprises redox-matching the nanoscopic pathway with the nanoscopic switch.

67. The method of claim 66, wherein the redox-matching comprises adjusting an  
30 electrochemical potential applied to the nanoscopic pathway.

77. The method of claim 75, wherein the detection sites are positioned in the nanoscopic pathway.

78. The method of claim 75, wherein the detection sites comprise nanoscopic switches.

79. The method of claim 75, wherein the detection sites comprise redox-active species.

80. The method of claim 75, wherein each detection site comprises a metal ion.

81. The method of claim 75, wherein the nanoscopic pathway is conducting at a defined electrochemical potential range.

82. The method of claim 75, further comprising redox-matching the nanoscopic pathway with the detection site prior to the activating.

83. The method of claim 82, wherein the redox-matching comprises adjusting an electrochemical potential applied to the conduction pathway.

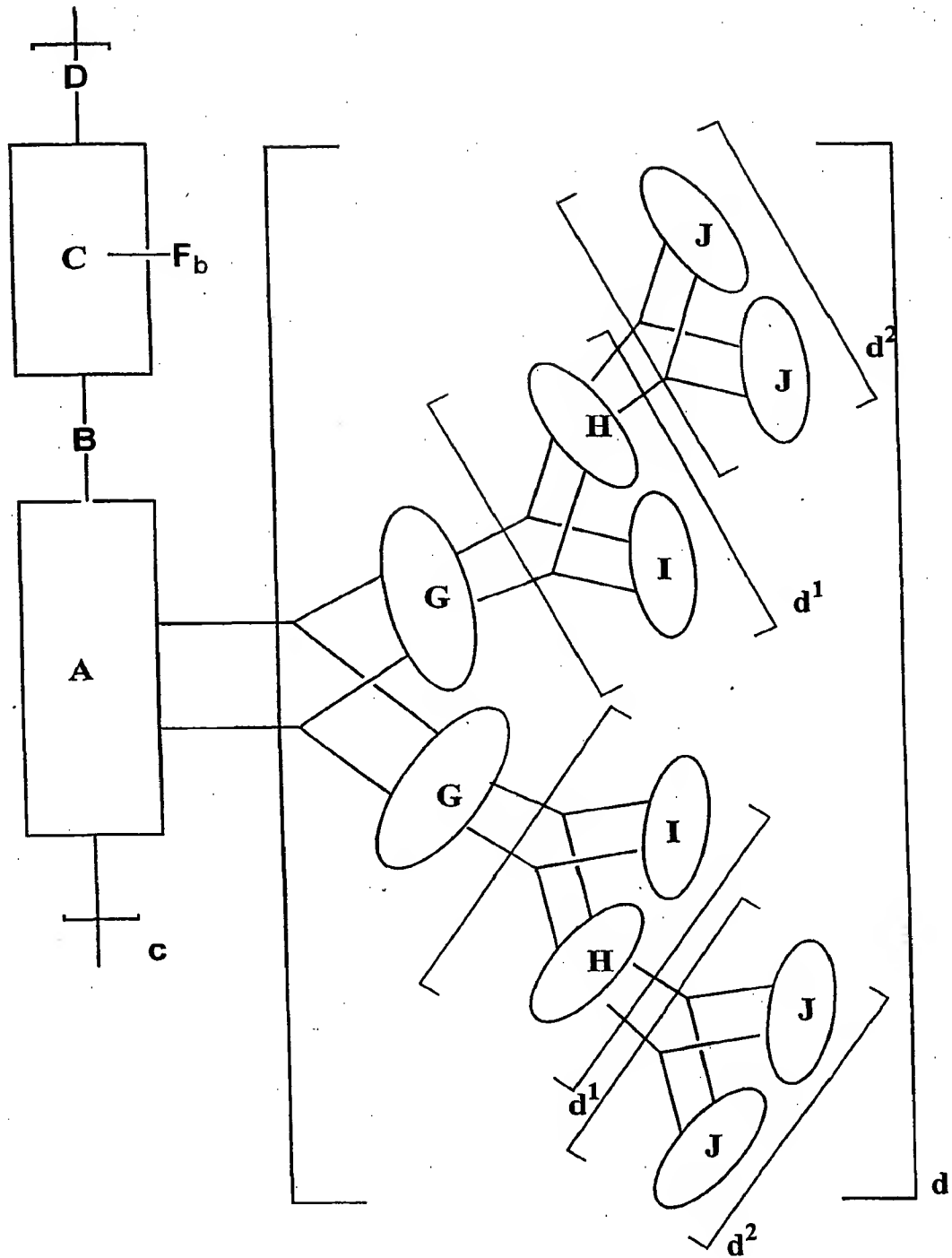
84. The method of claim 82, wherein the detection site is a metal ion and the redox-matching comprises adjusting a ligand environment around the metal ion.

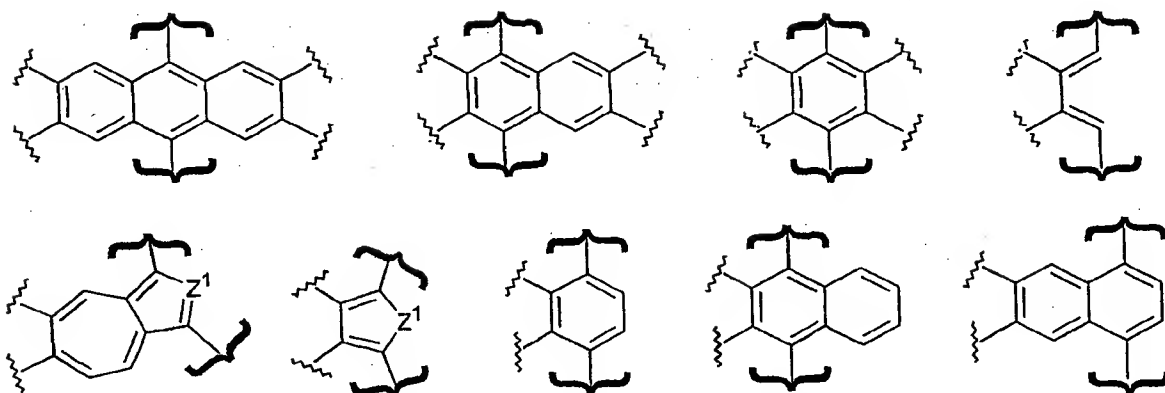
85. The method of claim 76, wherein the binding event causes the nanoscopic pathway and the detection site to be redox-matched.

86. The method of claim 85, wherein the detection site comprises a metal ion complex and the binding event occurs between the complex and the analyte.

87. The method of claim 75, wherein the nanoscopic pathway is selected from the group consisting of an organic group, an organometallic compound, a coordination compound, a nanoparticle and a biological species.

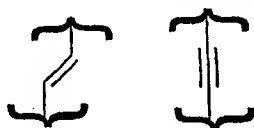
100. A method for amplifying conductivity, comprising:  
providing an article comprising a nanoscopic pathway;  
positioning a plurality of nanoscopic switches in the article; and  
activating a number of the plurality of nanoscopic switches, the number being greater  
5 than a percolation threshold.
101. A method for reducing conductivity, comprising:  
providing an article comprising a nanoscopic pathway;  
positioning a plurality of nanoscopic switches in the article; and  
10 deactivating a number of the plurality of nanoscopic switches, the number being less  
than a percolation threshold.
102. A method for detecting the presence of an analyte, comprising:  
providing an article comprising a nanoscopic pathway;  
15 positioning a plurality of nanoscopic switches along the nanoscopic pathway; and  
activating a number of the plurality of nanoscopic switches, the number being greater  
than a percolation threshold.
103. A method for detecting the presence of an analyte, comprising:  
20 providing an article comprising a nanoscopic pathway;  
positioning a plurality of nanoscopic switches along the nanoscopic pathway; and  
deactivating a number of the plurality of nanoscopic switches, the number being less  
than a percolation threshold.
- 25 104. A method for synthesizing a conducting polymer, comprising:  
providing a monomer having a first and second polymerization site;  
polymerizing the monomer at the first site to produce a first polymer; and  
polymerizing the monomer at the second site to produce a second polymer, the second  
polymer isolating the first polymer.  
30
105. A block co-polymer, comprising:  
blocks of a conducting material; and





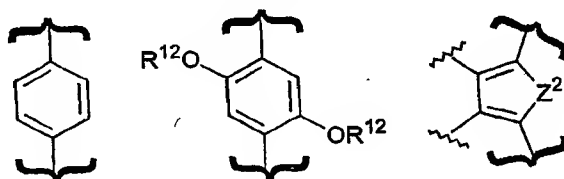
wherein any hydrogen in A can be substituted by  $R^5$ ,  $R^5$  is selected from the group consisting of  $C_1$ - $C_{20}$  alkyl, aryl,  $C_1$ - $C_{20}$  alkoxy, phenoxy,  $C_1$ - $C_{20}$  thioalkyl, thioaryl,  $C(O)OR^6$ ,  $N(R^6)(R^7)$ ,  $C(O)N(R^6)(R^7)$ , F, Cl, Br,  $NO_2$ , CN, acyl, carboxylate, hydroxy;  $R^6$  and  $R^7$  can be the same or different and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl, and aryl;  $Z^1$  is selected from the group consisting of O, S and  $NR^8$  and  $R^8$  is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl, and aryl;

B and D can be the same or different and each is selected from the group consisting of:



wherein any hydrogen in B and D can be substituted by  $R^9$ ,  $R^9$  is selected from the group consisting of  $C_1$ - $C_{20}$  alkyl, aryl,  $C_1$ - $C_{20}$  alkoxy, phenoxy,  $C_1$ - $C_{20}$  thioalkyl, thioaryl,  $C(O)OR^{10}$ ,  $N(R^{10})(R^{11})$ ,  $C(O)N(R^{10})(R^{11})$ , F, Cl, Br,  $NO_2$ , CN, acyl, carboxylate, hydroxy,  $R^{10}$  and  $R^{11}$  can be the same or different and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl, and aryl;

C is selected from the aromatic group consisting of:



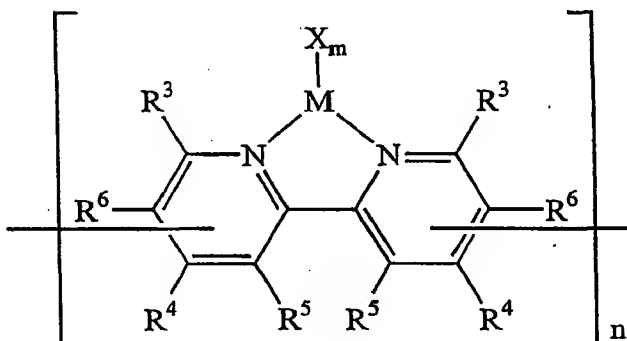
wherein  $R^{12}$  is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl and aryl; any hydrogen in C can be substituted by F which is represented by  $R^{13}$ ,  $R^{13}$  is selected from the group consisting of  $C_1$ - $C_{20}$  alkyl, aryl,  $C_1$ - $C_{20}$  alkoxy, phenoxy,  $C_1$ - $C_{20}$  thioalkyl, thioaryl,  $C(O)OR^{14}$ ,  $N(R^{14})(R^{15})$ ,  $C(O)N(R^{14})(R^{15})$ , F, Cl, Br,  $NO_2$ , CN, acyl, carboxylate, hydroxy;  $R^{14}$  and  $R^{15}$  can be the same or different and each is selected from the group consisting of



C<sub>1</sub>-C<sub>10</sub> heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I, and m = 0 - 3.

111. The article of claim 109, wherein the structure comprises a 1-, 2- or 3-dimensional array of n monomer units.

112. The article of claim 3, wherein the conducting polymer has a structure comprising the formula:



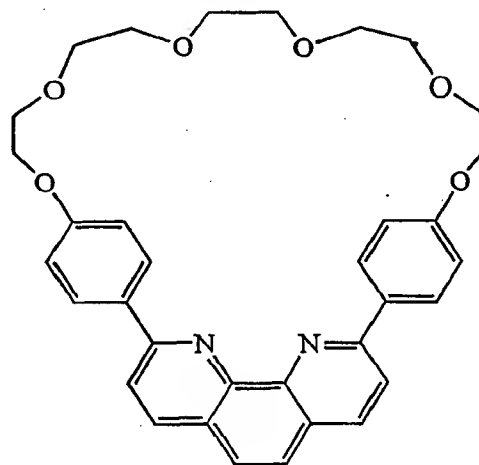
wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, and the polymeric structure comprises linkages through at least one of any R<sup>3</sup> - R<sup>6</sup> units or X and R<sup>3</sup> - R<sup>6</sup> can be the same or different, and each is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>10</sub> alkyl, C<sub>1</sub>-C<sub>10</sub> heteroalkyl, aryl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —COOR<sup>1</sup>, —CO<sub>2</sub>C(R<sup>1</sup>)<sub>3</sub>, —CONC(R<sup>1</sup>)<sub>2</sub>, cyano, nitro, hydroxy, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, —NR<sup>1</sup>COR<sup>2</sup>, thioalkyl, thioaryl, —SO<sub>2</sub>R<sup>1</sup>, —SOR<sup>1</sup>, —SO<sub>2</sub>OR<sup>1</sup>, F, Cl, Br, I, or where possible, any two R groups combining to form a ring structure; R<sup>1</sup> and R<sup>2</sup> can be the same or different, and each is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>10</sub> alkyl, C<sub>1</sub>-C<sub>10</sub> heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I; and X is selected from the group consisting of alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl and optionally interrupted or terminated by N, O, P, S, heteroalkyl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —COOR<sup>1</sup>, —CO<sub>2</sub>C(R<sup>1</sup>)<sub>3</sub>, —CONC(R<sup>1</sup>)<sub>2</sub>, cyano, alkyloxy, aryloxy, hydroxy, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, —NR<sup>1</sup>COR<sup>2</sup>, thioalkyl, thioaryl, —SO<sub>2</sub>R<sup>1</sup>, —SOR<sup>1</sup>, —SO<sub>2</sub>OR<sup>1</sup>, F, Cl, Br, and I; R<sup>1</sup> and R<sup>2</sup> can be the same or different, and each is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>10</sub> alkyl,

a conductive nanoscopic pathway, and  $n$  is an integer greater than 0.

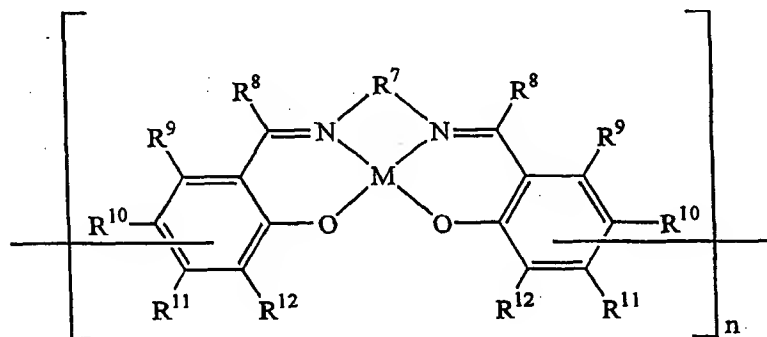
116. The article of claim 115, wherein the continuous chains of atoms comprises chains of methylene units optionally interrupted by an atom selected from the group consisting of oxygen, nitrogen, sulfur and phosphorus.

117. The article of claim 116, wherein the continuous chains comprise chains of ethylene

118. The article of claim 3, wherein  $X$  comprises the formula:




119. The article of claim 3, wherein the conducting polymer has a structure comprising the formula:



15 wherein  $M$  is a metal ion,  $n$  denotes a number of monomer units,  $n$  being at least 3, the polymeric structure comprising linkages through at least one atom in  $R^7 - R^{12}$  units, and  $R^7 - R^{12}$  can be the same or different, and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{10}$  alkyl,  $C_1$ - $C_{10}$  heteroalkyl, aryl, heteroaryl, carbonyl, acyl, acyloxy,  $-CHO$ ,

thioalkyl, thioaryl,  $\text{—SO}_2\text{R}^1$ ,  $\text{—SOR}^1$ ,  $\text{—SO}_2\text{OR}^1$ , F, Cl, Br, and I;  $\text{R}^1$  and  $\text{R}^2$  can be the same or different, and each is selected from the group consisting of hydrogen,  $\text{C}_1\text{—C}_{10}$  alkyl,  $\text{C}_1\text{—C}_{10}$  heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I, and  $m = 0\text{—}2$ .

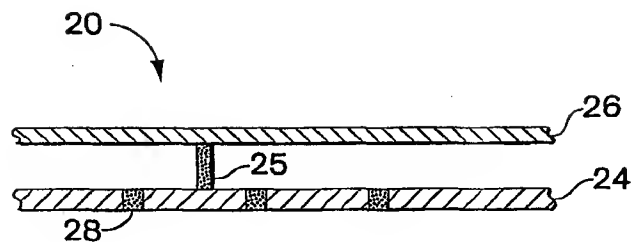
5 123. The article of claim 122, wherein the structure comprises a 1-, 2- or 3- dimensional array of  $n$  monomer units.

124. The article of claim 122, wherein the four  units comprise a macrocycle.

10 125. The article of claim 124, wherein the macrocycle is selected from the group consisting of cyclams, phthalocyanines and porphyrins.

126. The article of claim 124, wherein the metal ion is a transition metal ion.

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AGGREGATE

Fig. 3A

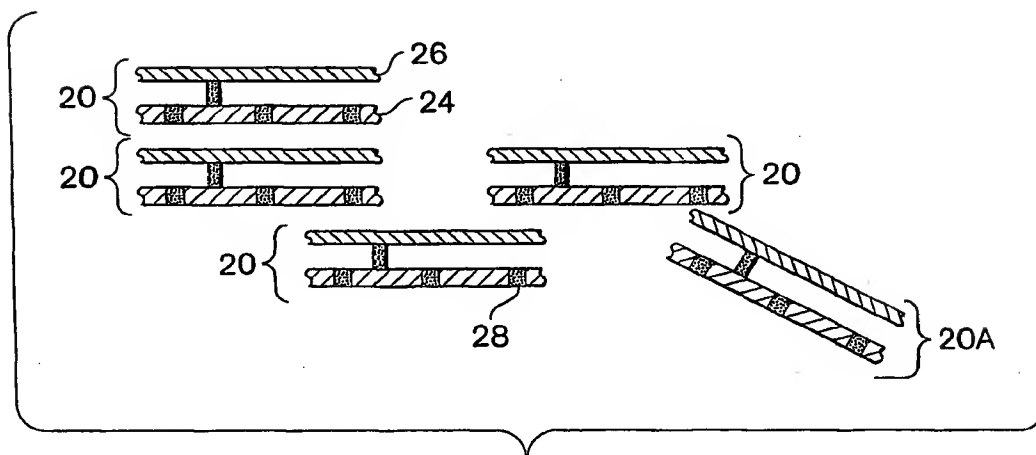


Fig. 3B

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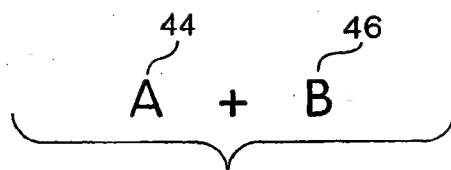
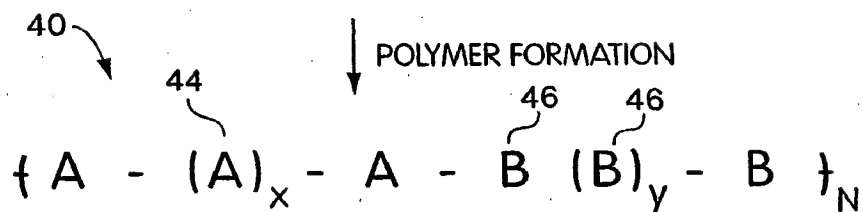


Fig. 5A



$N = 1$  or more than 1

Fig. 5B

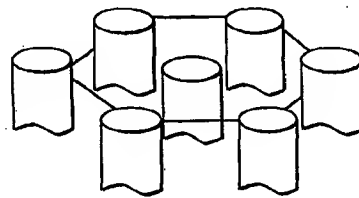
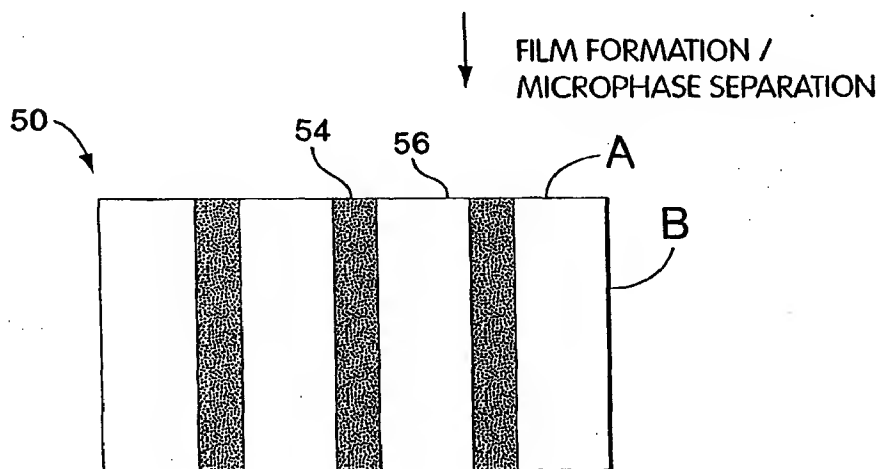


Fig. 5C

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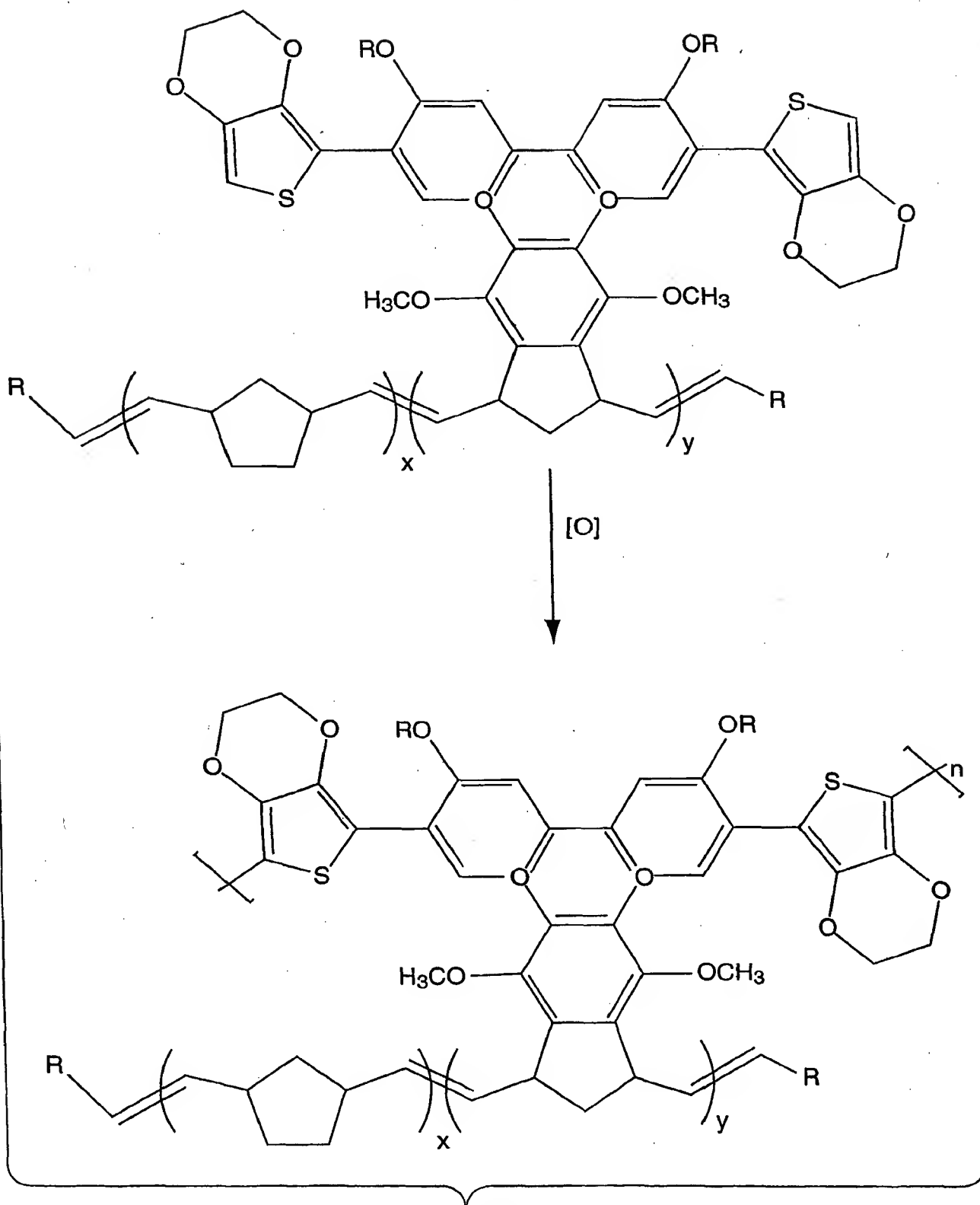


Fig. 6B

SUBSTITUTE SHEET (RULE 26)

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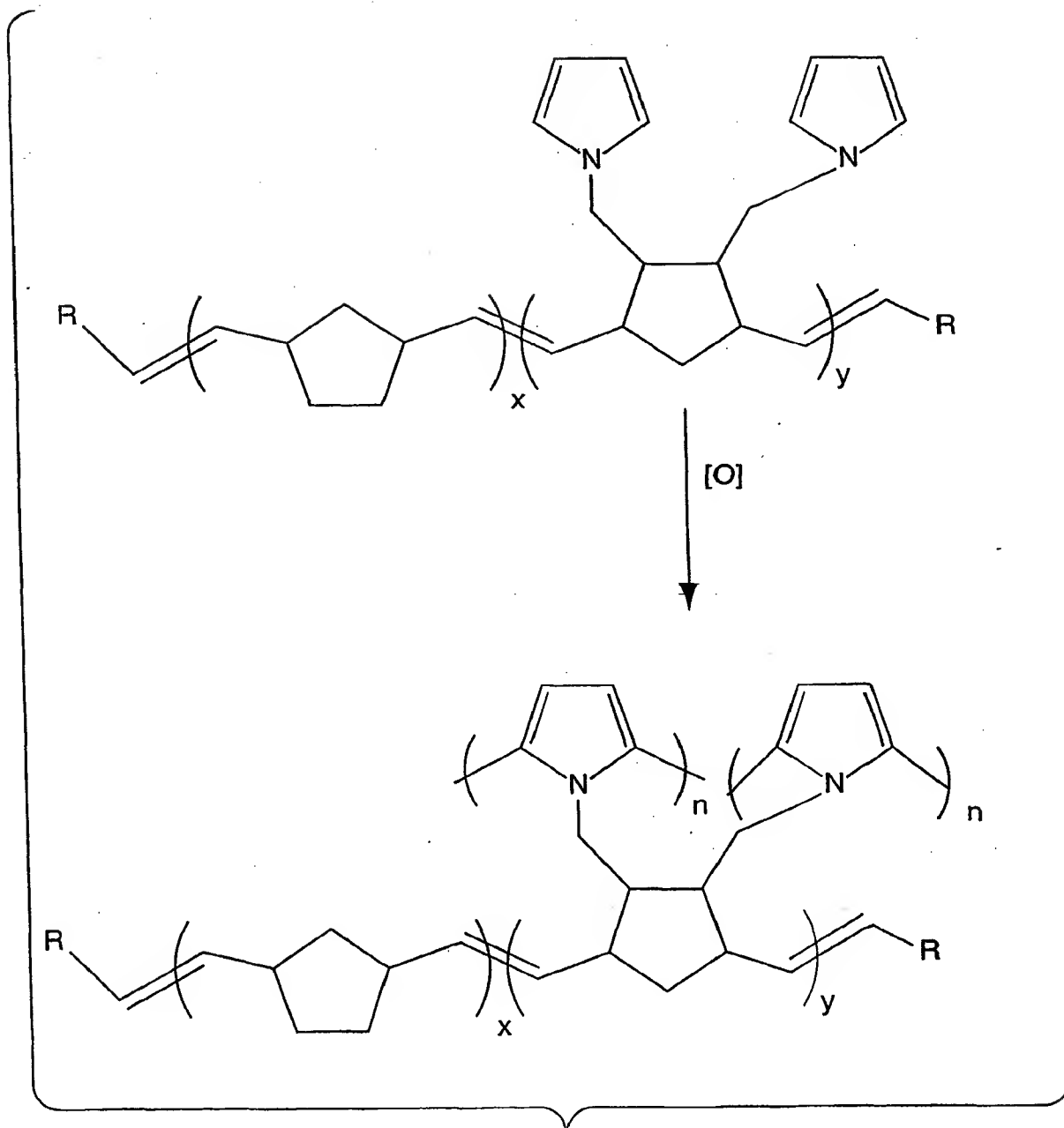


Fig. 8

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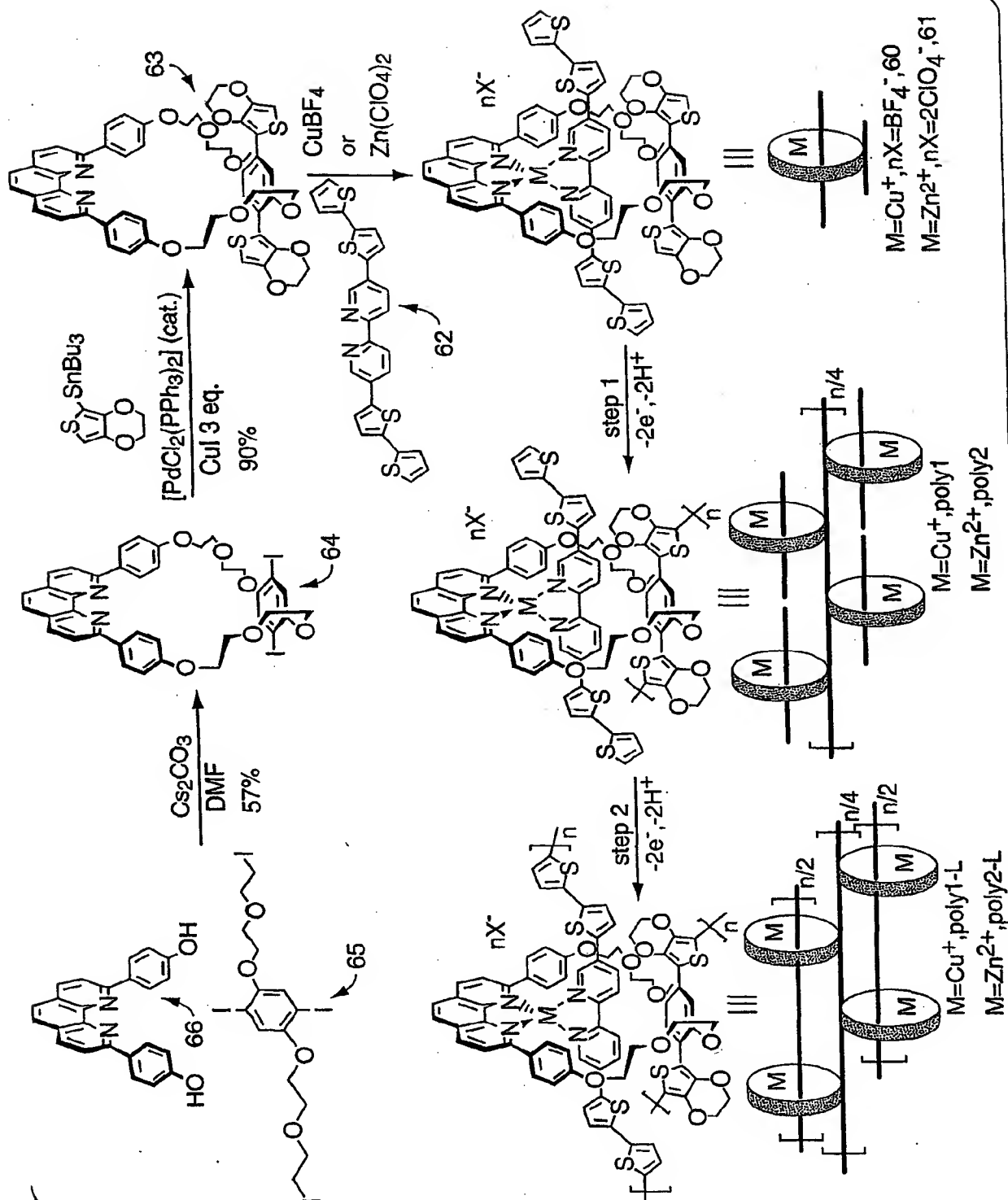


Fig. 10



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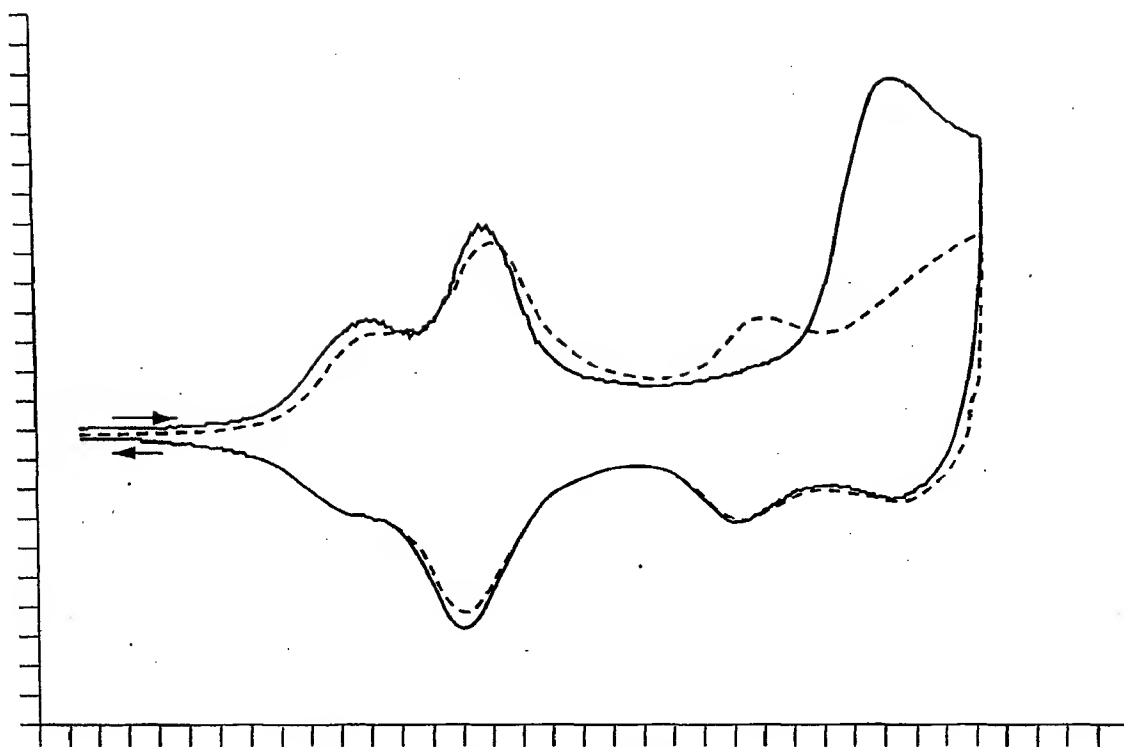


Fig. 11C

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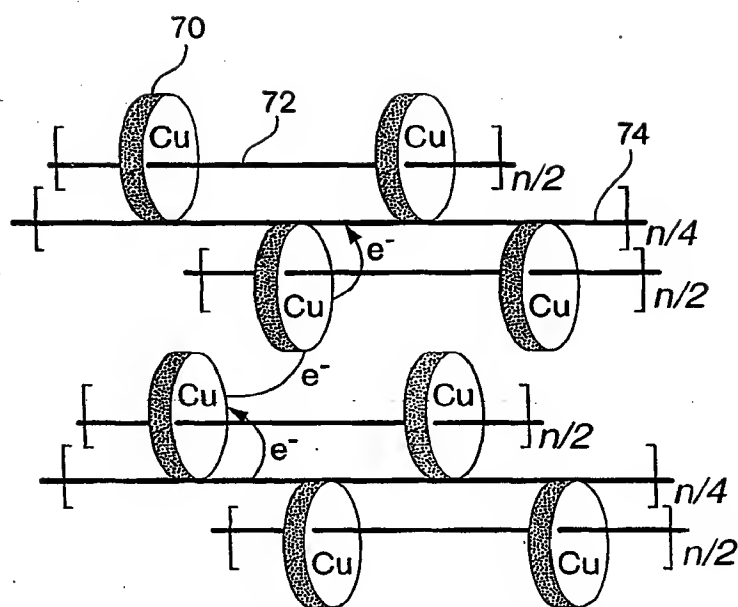


Fig. 13

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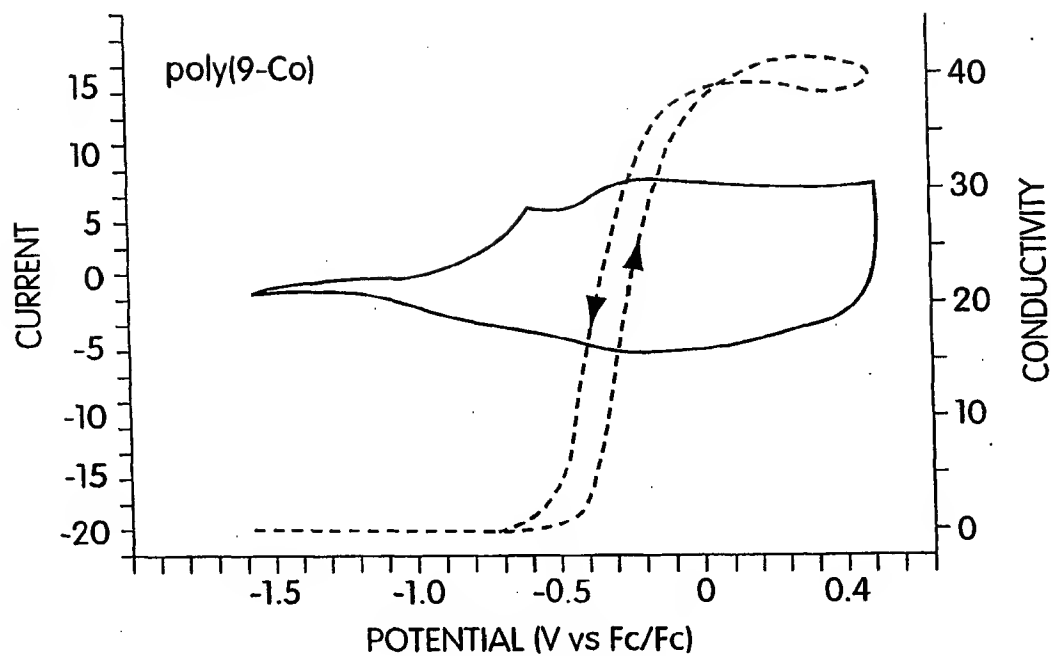


Fig. 15A

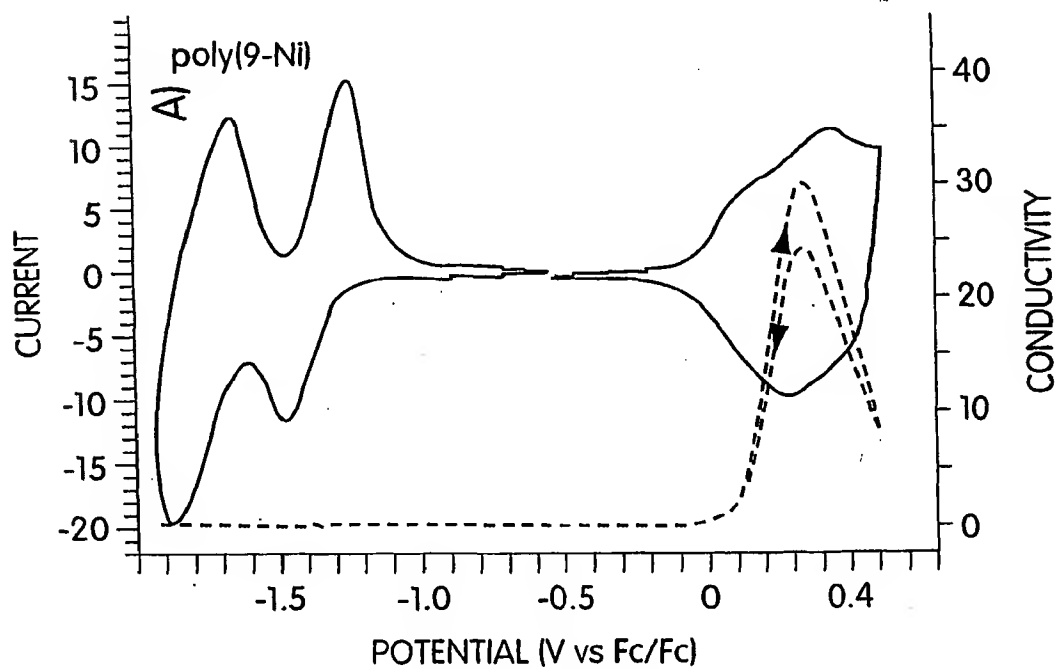


Fig. 15B

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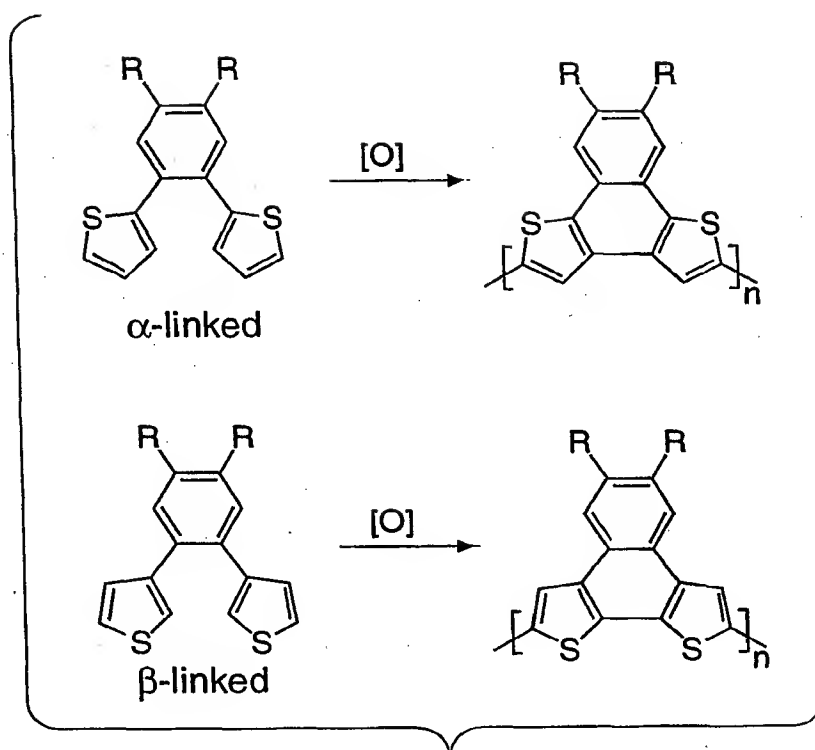


Fig. 17

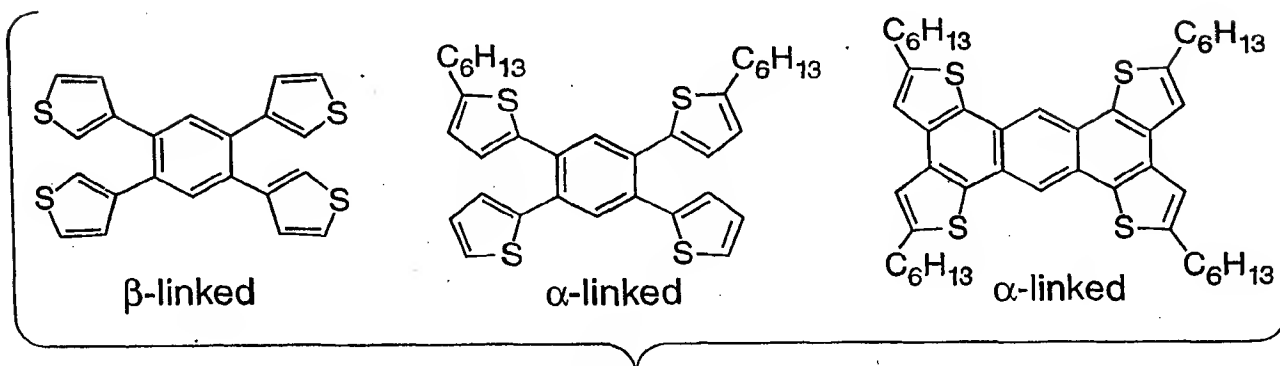


Fig. 19

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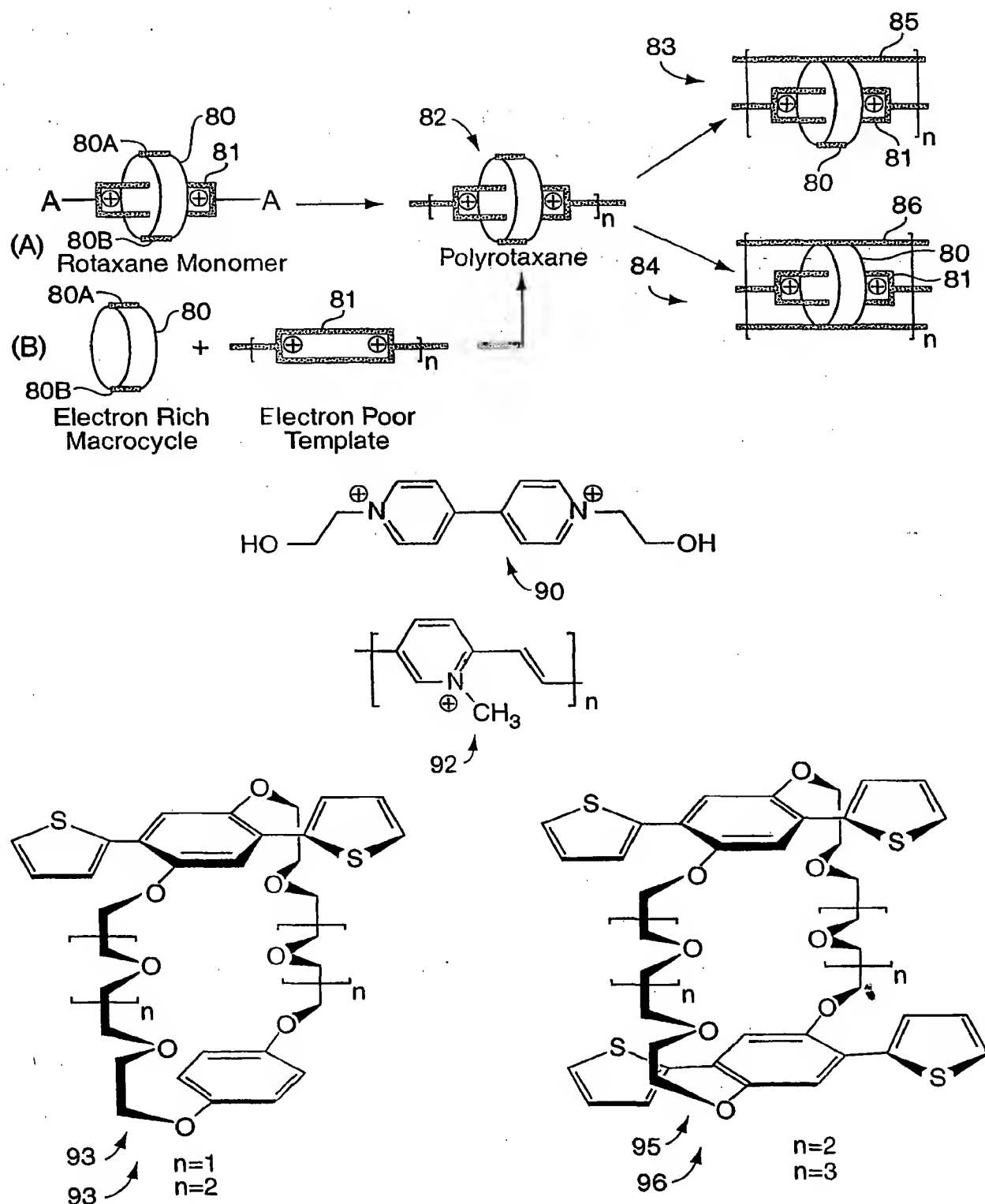


Fig. 20

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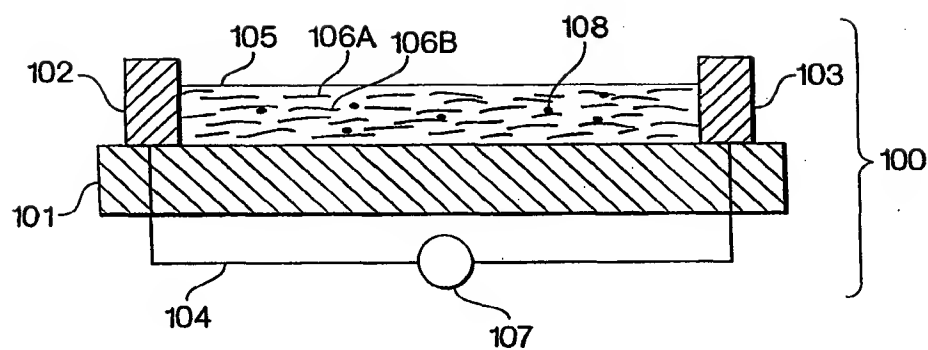


Fig. 22  
(Prior Art)

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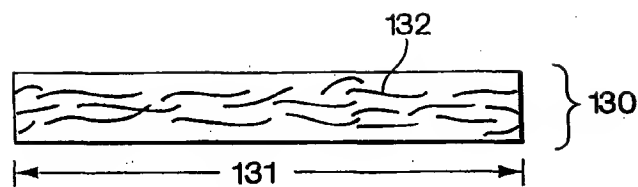
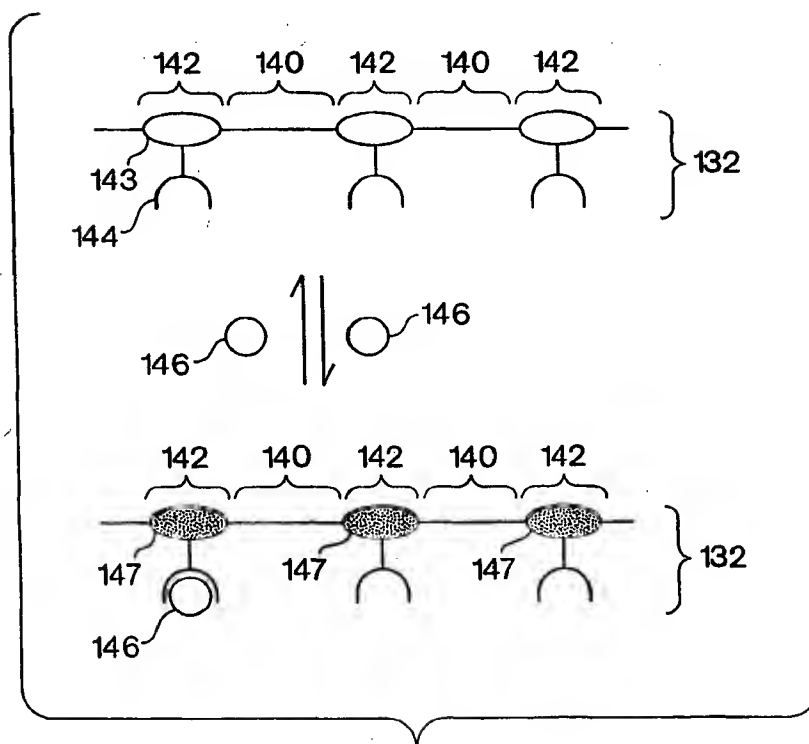


Fig. 24

Fig. 25  
(Prior Art)

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/03784

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08L101/12 H01B1/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C08L H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 57222 A (MASSACHUSETTS INST TECHNOLOGY) 11 November 1999 (1999-11-11)  claims	1-4, 55, 56, 59-61, 75, 87-89, 100-103, 106-109, 111
X	US 6 020 426 A (HIGASHI TAKETOSHI ET AL) 1 February 2000 (2000-02-01) claims 1,9	104, 105
X	WO 00 05774 A (MASSACHUSETTS INST TECHNOLOGY) 3 February 2000 (2000-02-03) claims 1,12 page 13, line 27 -page 14, line 2 -/-	105

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

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Date of the actual completion of the International search

28 June 2001

Date of mailing of the International search report

06/07/2001

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**INTERNATIONAL SEARCH REPORT**  
 Information on patent family members

International Application No  
**PCT/US 01/03784**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9957222 A	11-11-1999	EP 1080162 A	07-03-2001
US 6020426 A	01-02-2000	JP 10182760 A JP 11052594 A	07-07-1998 26-02-1999
WO 0005774 A	03-02-2000	AU 5320199 A	14-02-2000
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